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Room and Low Temperature Luminescence Properties of $CaSO_4$:Dy,Tm Codoped with Li

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Abstract

Rare earths, especially Dy or Tm doped $CaSO_4$ phosphors are actively studied. They have high sensitivity, a large dynamic range, thermal stability and ease of preparation. Nevertheless, they can be enhanced by inclusion of lithium and this study reports some effects of lithium co-dopant on the TL and radioluminescence (RL) emissions of two TL phosphors. Addition of Li as a co-dopant ion was made either during chemical preparation of the phosphors, or as a binder component mixed with the basic phosphors matrix during the process of pressing and sintering the TLD pellets.

Keywords: Luminescence; $CaSO_4$:Dy,Tm

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Introduction

Calcium sulphate doped with dysprosium or thulium are excellent thermoluminescent phosphors in radiation dosimetry due to their high sensitivity, relatively simple structure, good chemical, thermal and physical stability. It is well known that even very small quantities of lithium co-doping during the preparation of the different luminescence materials frequently plays an important role in the enhancement of luminescence efficiency [1]. There is ongoing interest in phosphor thin films in recent years because of the promise for application in display devices [2-3]. However, a systematic study of Li co-dopant on the thermoluminescence of some commonly used TL materials, with the exceptions of $CaSO_4$:Dy/Tm) was not performed [4]. We have recently shown that the addition of Li into some TL phosphors induces an enhancement in a lower temperature peak which is correlated with the increase of TL sensitivity. The high TL output of these TL phosphors could be used in dosimetric practice for special short-term measurements [5].

Experimental

The addition of Li ion as a co-dopant is performed during the procedure of chemical preparation of TL phosphors, or as the binder component mixed with basic phosphor matrix during the process of pressing and sintering the TLD pellets. Li was not added during the process of crystallization, but during the pressing and sintering of TLD pellets. Added Li compounds were Li_2CO_3, LiCl, LiF, $Li_2B_4O_7$ and Li_2SO_4. These TL phosphors are prepared by Dr. M. Prokić at the Institute of Nuclear Sciences-Vinca, Belgrade, Serbia [5].

A high sensitivity thermoluminescence system of Sussex University was used to collect TL signal from 25 to 280 K. The detail of this TL spectrometer has been reported elsewhere [6]. The $6K.min^{-1}$ heating rate was selected during the measurements to avoid the temperature

gradients between the heater strip and the emissive surface of the dosimeter. X-rays were used as the irradiation source. All samples were irradiated with a radiation dose of 5Gy at 25 K.

Results and Discussion

Although $CaSO_4$ thermoluminescence dosimeters have been routinely used in practice there are still many problems in understanding the details of the processes of the TL characteristics of the peak structure and spectra related to optimization. Consequently all models of the TL emission mechanics are quite speculative.

Figure 1 shows an isometric plot of the TL spectra of $CaSO_4$:Dy,Li at low-temperature. Similar spectra are observed during high temperature TL. The prominent peaks correspond to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition at 470 nm and the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ at 570 nm of Dy^{3+}. The Li ion induces small spectral shifts to shorter peak wavelengths compared with $CaSO_4$:Dy samples.

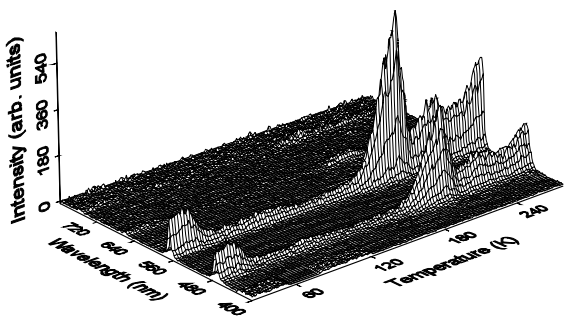

Figure 1. Isometric TL plot of $CaSO_4$:Dy,Li at low temperature following 5 Gy X-ray irradiation

Figure 2 shows radioluminescence data during heating (RTL) for $CaSO_4$:Dy,Li. The RTL spectra are not exactly the sum of RL (as seen during cooling) and TL, as was initially expected. Differences in peak temperatures and intensity between TL and RTL must be due to the dynamic excitation of the RL. It is possible that RTL is generating electrons and holes as well as filling trapping sites, whereas the TL only generates recombination with charges, which were previously trapped. The presence of the high hole concentration during RTL thus gives more intense light (x200) and radically modifies the trapping situation for the peaks near 200 K. One might assume that continuous excitation of RTL could just broaden the high temperature tail of the peaks, relative to TL, but in practice the 200 K features occur at higher temperatures. The lowest temperature peak is also poorly defined in RTL data.

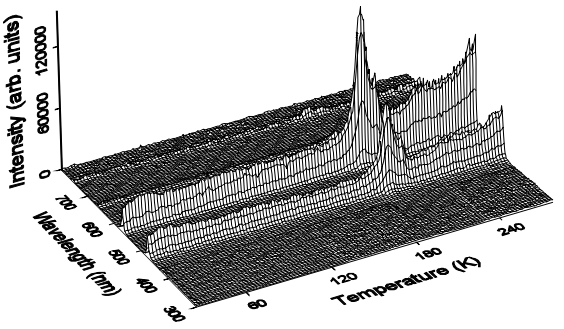

Figure 2. Radioluminescence spectra of $CaSO_4$:Dy,Li taken during heating (RTL) while irradiating by a X-ray source delivering dose rate of 10 $Gy.min^{-1}$.

Figure 3 shows an isometric plot of the RTL spectra of $CaSO_4$:Tm,Li at low-temperature. One often observes more intense emissions during RTL because of the high electron and hole density, which may be spatially correlated in pairs suitable for luminescence production. Although there was not intense emissions in the normal region of interest, experiments revealed some interesting results. Signals near 620 nm, and at longer

wavelengths, differ significantly from the expected Tm emission lines. They decrease slightly with increasing temperature and are undetectable above ~185 K. As is apparent from figures 3 and 4 the 620 nm region has several narrow line components which have slightly different temperature dependence within the most intense region, but figure 4 also clearly indicates a number of other components in the range to about 780nm. This major feature is clearly observed in the RTL plot of Tm and Li doped $CaSO_4$. These red emission lines appear in the Li doped material but do not match cited spectra of either Li or Tm. An obvious potential candidate for their origin is from fluorine. LiF is used in the sample preparation and F has a particularly intense set of emission lines precisely in the region of interest with the strongest features being near 624, 635 and 641 nm, but with other strong lines which closely match the observed spectral features up to ~ 775 nm. Therefore, whilst it is difficult to identify the details of the emission sites it seems clear that fluorine is providing an efficient luminescence centre, perhaps in combination with other intrinsic imperfections and the Tm and Li dopants. The reason for the disappearance above 185 K suggests that an intrinsic defect site is involved which anneals by 185 K. This could also explain why the signal is obvious in RTL but not in TL. The RTL does not represent a conventional glow curve but offers excitation of electrons and holes even in temperature regimes where TL does not release both types of charge.

These results may be interpreted by the process of energy transfer between host lattice defects and rare earth ions and a luminescence site involving fluorine.

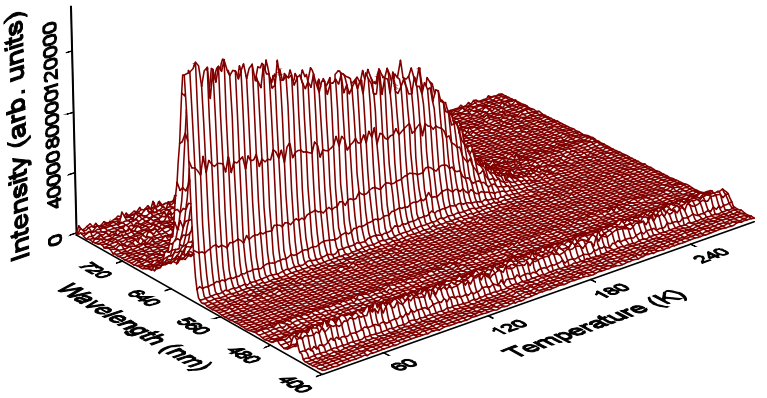

Figure 3. Isometric plot of $CaSO_4$:Tm,Li at low temperature while irradiating by a X-ray source delivering dose rate of 10 $Gy.min^{-1}$.

In the spectral example selected for figure 4 one can recognize a number of the Tm line transitions as well as the unusual feature previously discussed in terms of a fluorine impurity site. RL spectra are shown for $CaSO_4$:Tm,Li at 280 K and 25 K. In this example emission lines at 340 nm ($^3P_0 \rightarrow {}^3H_4$) and 360 nm ($^1D_2 \rightarrow {}^3H_6$) give the same intensity level at both temperatures, but 455 nm ($^1D_2 \rightarrow {}^3H_4$) emissions are relatively more intense at 280 K than at 25 K. Note that there is a small movement of the line position. Structure in the peak envelope near 642 nm emission is apparent, as are other weak peaks up towards 770 nm.

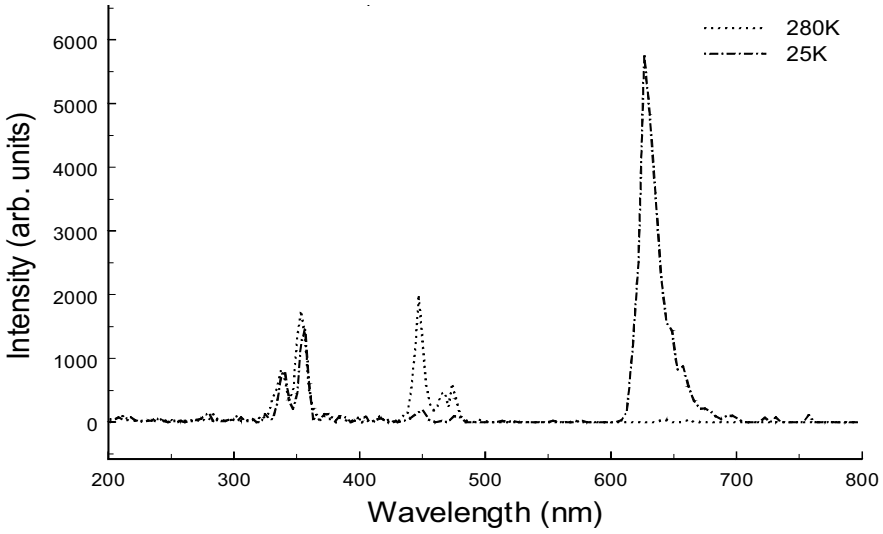

Figure 4. Radioluminescence spectra of $CaSO_4$:Tm,Li at 280 and 25 K.

Conclusion

The addition of lithium to the rare earth doped $CaSO_4$ enhances the overall luminescence efficiency of the material, which is of definite interest for yet further improvements in the dosimetric TL phosphors. There are clearly some fundamental differences in low temperature signals excited only by heating (TL) or those continuously excited (RTL). The latter shows features linked to TL superposed on an RL base line. However, the continuous excitation slightly shifts the apparent peak temperatures. In the Li doped material there were strong red emissions with features characteristic of fluorine impurities. This is not unreasonable since LiF is used in the process of Li doping. The F signal is apparently linked to other defect components as the signal is inhibited above 185 K.

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